Environmental Remediation of Contaminated Sites
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Lecture - 38
Diffusion of Contaminant through Solidified Form

Hello everyone. So again welcome back. Let us continue our discussion regarding the solidification and stabilization of relevant aspects. So we are going to move on to relatively more technical aspects, as in we looked at the relevant aspects has in what is going to happen to the contaminant during solidification and stabilization, how can it be transported and so on and so forth right and we are looked at obviously you know physical transport and diffusive transport.

Physical transport again, we looked at I believe hydraulic conductivity, 10 power -5 to 10 power -8 typically, let us say right, again depends obviously on the porosity too. Porosity you can estimate from the water to the cement ratio as typically let us say water to cement ratio -0.1 as an water to cement ratio is 0.5, then the porosity will typically be around 0.4 now. Again different aspects and then we started discussion regarding leaching now right. So what is this about?

So let us say, I have pore space in my relevant solidified and stabilized mass and within that pore space, I have water and you know I have the compound are you know they are contaminant in that aqueous phase let us say and even though there is no advection as in you know the water is not flowing through let us say, but this particular contaminant let us say if it is not contaminant, this solid let us say or solidified and stabilized mass or block let us say is in contact with water or leachate let us say right. So let me try to represent that here.

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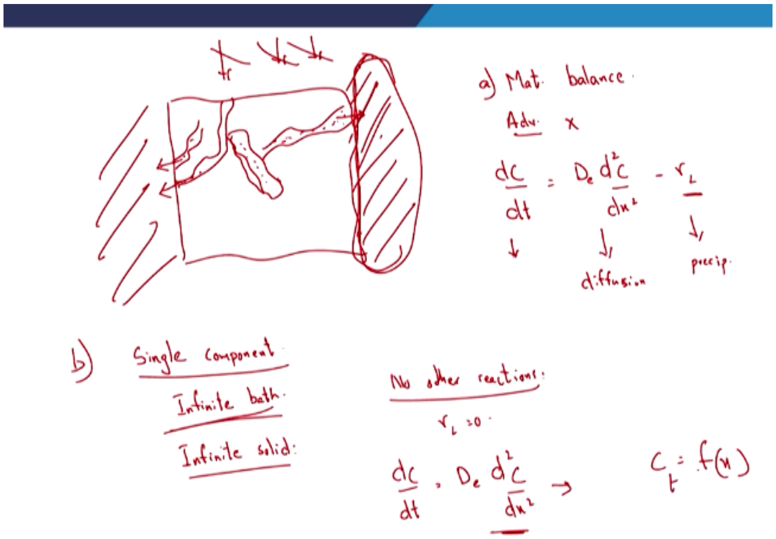

a) Mat. balance

Adv. ×

$$\frac{dc}{dt} = D_e \frac{d^2c}{dx^2} - r_L$$

diffusion

precip.

b) Single component

Infinite bath

Infinite solid

No other reactions

$r_L = 0$

$$\frac{dc}{dt} = D_e \frac{d^2c}{dx^2} \rightarrow C_t = f(x)$$

So this is my solidified and stabilized block. You know I am just drawing that as a block, but it need not be and let us say I am going to have pores within it and within this pore, let us say I am going to have the contaminant you know dissolve in the water or in the aqueous phase, so even though there is no net flow, let us say, when advection is run we have net flow and this contaminant is flowing along with this water let us say.

Even though there is no such flow and let us say so there is mass of your, so there is no flow, but let us say this mass of your, solidifies and stabilized block let us say is in contact with leachate let us say. You have some leachate here let us say and as you know and assume that this is the leachate and it is in contact with the leachate. So what is going to happen here or how can the compound be transported as we discussed, it can be transported by diffusion.

Why is that because there is no contaminant in this leachate right and there is dissolved contaminant within the pore space now right. So obviously due to diffusion it can or it low and you know if there is obviously the leachate here too and this is the pore space right, your compound is going to diffuse out right. So let us try to see how we can try to understand how much will leach out and so on and so forth, that is something we always need to do right.

So again what is the approach here, it is based on material balance. So we are going to look that mass balance or material balance. So here let us say do we have any advection term here, no right. We are assuming that the transport is only driven by diffusion now right. So let us try to write the mass balance equation for that. We know that it is dc/dt is equal to the effective diffusion coefficient or dispersion coefficient.

Depending upon how we look at that and the second derivative let us say right and second derivative of concentration and any sources are seen, so let us say rate of loss is due to may be precipitation or saturation, right. Again keep in mind this diffusion only occurs when the contaminant is in the aqueous phase. It can change, it can go from let us say what do you say the water that is inside the solid to the leachate that is outside the solid through diffusion also.

Obviously it should be dissolved now right. So again this compound can also be undergoing any other reactions leading to its loss well even formation, but that is relatively rare in this scenario. So but even if its formation, you can write it accordingly by changing the particular sign, right. So let us say if the compound is being precipitated or such that needs to be taken into account. So this that let us say for example precipitation is occurring.

I am going to take into account the loss of that compound from that volume of water inside this particular pore space let us say by this rate of loss and this gives me the loss due to diffusion or the diffusion term, right and this obviously gives me how the concentration is changing with time let us say in this whole system of and what the system here the water in the pore space let us say. So again Bs so how do I go about that there are different models.

So single component, I am assuming that the contaminant is the only component of concern here and obviously I need to be able to assume some what do we say boundary conditions to be able to solve that. So we looking at the system what are some of the boundary conditions. We are going to assume that it is an infinite bath, as in the concentration we know outside this particular what do we say system let us say, outside the system is 0.

So it is an infinite bath as in the concentration in this region is 0 right and that it is an infinite solid. What does that mean that the concentration within the solid let us say is always the same and is always at the certain particular value now, even that a decent enough assumption especially assuming that you have considerable what do we say quantity out there and the loss is due to diffusion now let us see.

So what are the boundary conditions we are looking at that outside this particular mass that you are referring to the control volume let us say. You are assuming that it is an infinite bath or infinite dilution so the concentration is 0 outside the system and inside it is an infinite solid, right. So even though diffusion is taking place, the concentration of that relevant what do we say the compound or such is more or less C not or such, right.

So we are going to assume that and also assuming that there are no other reactions occurring. So we are assuming that no other reactions are occurring. So what is that mean that means the rate of loss equals 0. So from that I am going to end up with dc/dt or D equal to diffusion coefficient secondary to with respect to x and to solve this we will more or less get C as a function of x, right. So that is what you see here or C at time t is the function of x. So I have the solution I believe here in the next slide.

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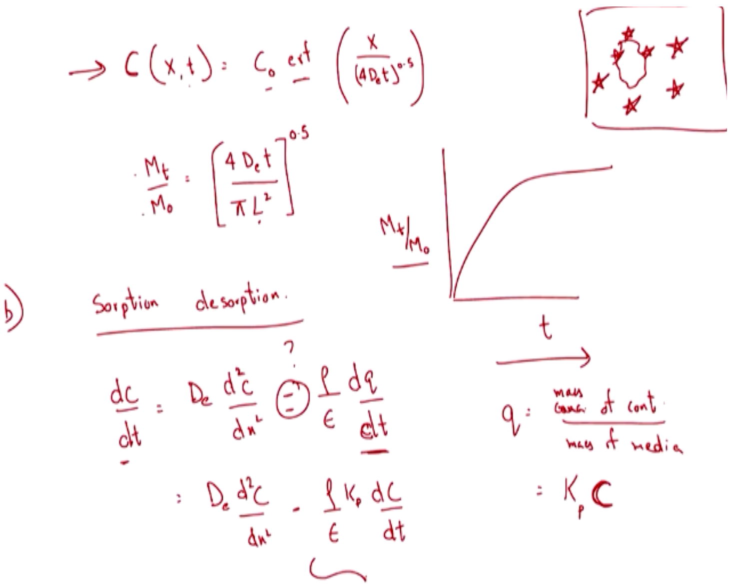

$$\rightarrow C(x,t) = C_0 \operatorname{erf}\left(\frac{x}{(4D_e t)^{0.5}}\right)$$

$$\frac{M_t}{M_0} = \left[\frac{4D_e t}{\pi L^2}\right]^{0.5}$$

b) Sorption desorption.

$$\frac{dc}{dt} = D_e \frac{d^2c}{dx^2} \overset{?}{\ominus} \frac{\rho}{\epsilon}\frac{dq}{dt}$$

$$= D_e \frac{d^2C}{dx^2} - \frac{\rho K_p}{\epsilon}\frac{dC}{dt}$$

$$q = \frac{\text{mass conc of cont}}{\text{mass of media}}$$

$$= K_p C$$

So it looks like if you solve that we get that concentration at x,t C not error function of x/square root of 4Det. So again transforming that into variables that we need which is mass that has leached out by initial mass=the square root of 4Det/pi L square, right. 4 diffusion coefficient time let us say pi and L is typically the length let us say that is perpendicular to your or know in the direction of diffusion let us say.

So that one aspect to look at and if its spherical or such. we look at total volume by total surface area and so on, so different ways but we will look that in greater detail. So this is what we have out or right, so let us try to see how that happens. You know something like this let us say, the mass that leached out right as time keeps increasing, let us say, right. Here we have Mt/M not and with time as you see the profile more or less you know flattens out.

So why is that obviously it is because let us say overtime right. What happens now the concentration gradient decreases right. Again drives diffusion that you know we have region where the concentration is relatively higher and one region where concentration is relatively lower and you know the system wants to see to it that this is where the system finally ends up with, but obviously at this stage the relevant transport is relatively greater let us say.

And as we move to this particular state obviously right, the concentration gradient is less. So that is why you see let us say its affect on the relevant diffusion here, because the concentration is relatively less as you progress along with time, even though our assumptions were infinite solid that something that obviously happens out there. So again this is something to keep in mind right. So part B is when, let us say when we have adsorption or desorption, let us say.

Adsorption or desorption should be taken into account. For example, in the earlier case, we assume that there were no other reactions occurring and so on or there was no adsorption, desorption or precipitation so on. So we are not going to look at the case where we have the precipitation or the compound being removed from that what do we say water in the pore space by being precipitated out, but we are going to look at let us say adsorption or desorption, the relevant affects.

And this is something we did look at earlier, but let us just write that down, dc/dt is equal to again the diffusion coefficient or dispersion coefficient let us say and second derivative let us say of concentration –rho by bulk density by porosity and dq/dt, what is this q, q is nothing but the concentration of contaminant, not concentration, pardon me, mass of contaminant per mass of that media or it gives you an idea about the concentration of the contaminant adsorbed onto the media.

So the q will obviously be dependent upon concentration in the aqueous phase. For example, let us we know that let us say you have a solid here and the compound can either be in the aqueous phase or it can be adsorbed on to the solid now. How this is going to be depend upon let us say it obviously is going to be dependent upon the number of molecules or the concentration in the aqueous phase. So the greater the number typically in this aqueous phase.

So greater the concentration on the solid now. So q=KpC if you assume that it is a linear relationship, right. So I can plug this in here and this is something we looked at with respect to I believe mass transport or natural attenuation and so on and so forth. So I can plug this in here Kp*dc/dt and why is this negative here, because q, what is q, q is the mass of the contaminant per mass of the media. q increasing what does that mean if q increases C will decrease what is C.

C is the concentration in the water or water in the pore space. Q is the concentration around the solid now. So if concentration on solid is increasing, what will happen to the concentration of the relevant molecule in the water, it will obviously be decreased because where is the mass of the contaminant coming from, only from the water it is going to the or on to the solid now. So if q is decreasing what happens, it means that the compound is being desorbed.

So the contaminant is being you know is changing from being adsorbed and moving into the aqueous space. So that is why let us see dc/dt will have the opposite sign as dq/dt. So plugging this in and so on and so forth, let us see what we have. So we dc/dt and taking this term out to the left, again we do not need to mug stuff up.

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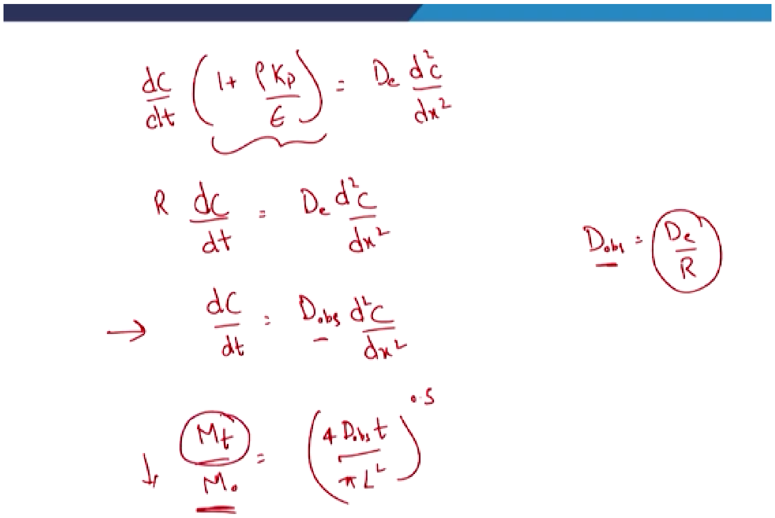

$$\frac{dc}{dt}\underbrace{\left(1+\frac{\rho K_p}{\epsilon}\right)} = D_e\frac{d^2c}{dx^2}$$

$$R\frac{dc}{dt} = D_e\frac{d^2c}{dx^2}$$

$$\underline{D_{obs}} = \boxed{\frac{D_e}{R}}$$

$$\rightarrow \frac{dc}{dt} = \underline{D_{obs}}\frac{d^2c}{dx^2}$$

$$\downarrow \underline{\boxed{\frac{M_t}{M_0}}} = \left(\frac{4D_{obs}t}{\pi L^2}\right)^{.5}$$

But we need to understand let us say where we are coming from let us say is equal to second derivative and thus obviously if you remember that is the retardation coefficient right. Now may be it seems familiar to the case when we looked at the case the case for natural attenuation and looked at trying to model the relevant scenario, right. So I am left with dc/dt=D absorbed. D absorbed is obviously De/R. So again this is similar to what we already had earlier here.

But instead of D effective diffusion coefficient or dispersion coefficient we will have the D absorbed. So again the relevant solution will be similar and we will end up with Mt/M not is equal to square root of let us look at what we have here, pi L square here 4D absorbed now into time I believe, okay. So that is what we see here, right. So this is the equation obviously, but let us try to understand this now. So what is the effect of having you know adsorption here, right.

In the early case, we assume that it was only diffusion out, but if you are also considering that the compound can be adsorbed on to the relevant media or the solidified and stabilized mass, so what can happen now think of that. So as in what is happening to D here or this term compared to what we had earlier. It is now De/R or you know its decreasing. So if this is decreasing what happens to Mt/M not now. It means that Mt/M not is also decreasing.

So that means that the effect of what do we say adsorption obviously decreases the mass that can leach out. Obviously it makes sense. Again I think about it logically and even if you look at in the equation. If we had no what we say adsorption, pardon me, it would not have been the D absorbed but just D effective diffusion coefficient, but now as we see we need to divide that by R meaning that D absorbed is going to be smaller than De or effective diffusion coefficient.

What does that mean or what is the effect that we can visualize from this equation that means that Mt/M not is smaller. Mt/M not is smaller, what is that mean that the mass leached out of certain time is lesser than the case, when there is no adsorption right. So that is something to keep in mind now right. So until now we have looked out single component models, right.

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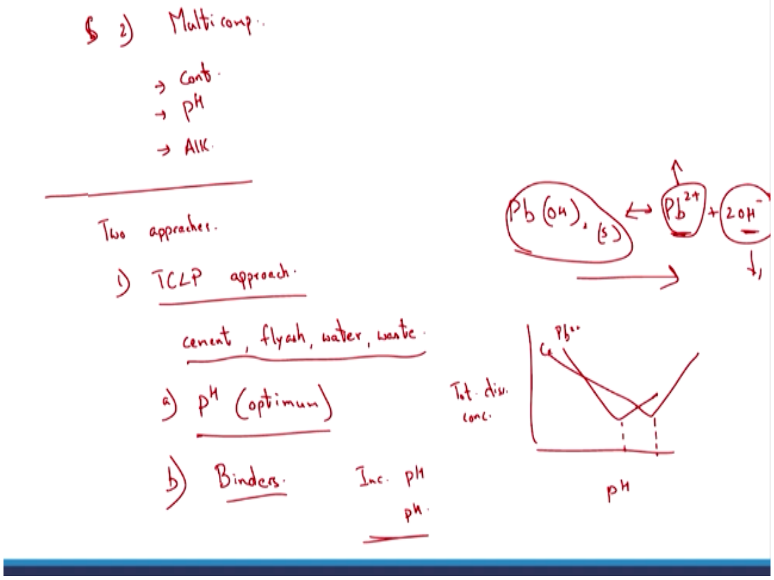

So than we can also have multicomponent models as in that and just looking at the contaminant, we can also have to look out the effect of pH, effect of alkalinity and so on and so forth, right. So we can have the relevant theoretical models right, but typically making the actual measurements when we are looking at multicomponent models and such is more worthwhile go way to go about the relevant aspects, right.

So now let us move onto how to get things done now. Let us say we understood what happens when so on and so forth but let us say now I want to solidify and stabilize certain waste. What are the aspects that I need to consider? I need to know how much waste, how much cement, how much flyash and how much water I need to put in, but what is my objective here. The objective is that I want to see to it that it cannot be classified or should not be classified as a hazardous waste or that you know it minimize the leaching.

So 2 ways what are they, 1 that you know it minimizes the actual harmful effects such that the leaching is minimum or such that you know if and when the relevant authority or you let us see conduct the TCLP test, it shows up that the relevant contaminant in the leachate are relatively less than the thresholds or after solidification and stabilization this waste is no more a hazardous waste. So there are 2 approaches, right. So 2 approaches here, what are they.

We will discuss the first 1. The first 1 is the TCLP approach right. So what this about? So we will let us say initially have your waste let us say Moradabad site and you have the relevant waste and you conducted the TCLP test and you saw that in your leachate or you know in the TCLP test leachate, you saw that the contaminant concentrations or concentrations of various heavy metals are very high and thus you have to classify that as hazardous waste.

Thus accordingly you will need to dispose that, but now let us say after you chose solidification and stabilization, so you solidified and stabilized that particular waste now let us say. Even after that obviously you need to conduct the TCLP test to check its effectiveness let us say. So after conducting the TCLP test again we are going to on the solidified and stabilized mass. How are we going to do that, we are going to first break down the solidified and stabilized mass to less than 9 mm size, if I am not wrong right, 9 mm size particle.

Then look at the relevant what we see extraction fluid that needs to be added depending on the pH and then we are going to add the acetic acid, right. We are going to add the acetic acid to bring down the pH to certain value and then let us it equilibrate as an endeavor and mixing for 24 hours. So what is the assumption here that, as I decrease the pH let us say the relevant contaminants will leach out into the leachate or we leach out into the relevant solution let us say.

But when I am looking at the TCLP approach what I am going to do? I am going to maintain the pH to be high enough that even after addition of this acetic acid, the pH is going to be at the optimum value, so that the heavy metals do not leach out into the relevant solution, makes sense hopefully. Let us try to understand that. It is like beating the test now, as in you prepare for, you are writing the test let us say to only pass the test not to learn the relevant aspect, let us say.

That is going to be relatively different to what the second approach, but here what the approach now. Your approach is to just beat the TCLP test. So if you conduct the test on the solidified and stabilized matrix, it is going to show that it is not a hazardous or cannot be classified as a hazardous waste. So what are the aspects obviously that we need to keep in mind or how do we go about it here, right. So let us look at the relevant aspects now.

So what do I need, obviously I need amount of cement, flyash if I am going to add that, water and waste. So we have to find these what do we say fractions. So what the approach here, again we are trying to beat the TCLP. So to beat the TCLP what do we need to look at, we need to find the optimum pH and how do we find this optimum pH obviously?

We are going to find the optimum pH such that even after addition of your extraction fluid or the acetic acid in your TCLP test, the pH will be high enough such that you know the relevant heavy metals will not leach out, right. For example, we know that for lead PbOH twice solid, it will dissolve into or be in equilibrium with Pb2+ and 2OH-, right. So this is what we have. So let us say in the TCLP test, we are adding the acid, what does that mean, we are decreasing OH-.

As this decreases, the system moves towards the right as in your PbOH twice the solid is going to dissolve now and now you are going to have higher concentrations of Pb2+ in your leachate, let us say, but to see to it that the Pb2+ concentrations do not cross a certain threshold what do you need to do? You will see to it that your OH- initially or the initial pH is high enough that even after decreasing the OH- or adding the acid, you are going to see to it that this Pb2+ final concentration will not be you know higher than the relevant thresholds.

So that is what we are saying when we are looking at pH or optimum pH right. We will look at that approach or calculations, pardon me and obviously in this case, I need to choose binders. So binders again typically cement, flyash and there are other binders too and again binders can have or you know can increase the pH or some of them can even decrease the pH. So we need to look at these aspects again and that is something we will take into account.

So again how are you going to add the binders, so let us say some of them can increase the pH, some of them can decrease the pH. So we will need to look at the fractions in such way that you end up with the optimum pH, right. So again keep in mind that let us see, as we looked at it for lead let us say. If this is the pH and this is total dissolved concentration, we saw that the profile is something like this for lead anyway, but for may be chromium, it can be something else.

So what I am trying to say is that there is no 1 particular optimum pH at which, let us say all your particular you know heavy metals are going to be you know precipitated out or such let us say or stay in the solid phase. So what do you do now, so depending upon let us say cost consideration let us say and relevant aspects, you are going to choose a range let us see or 1 particular optimum pH.

You are obviously not going to have 1 particular pH, but you can choose the optimum one and also to increase the range let us say where this pH is optimum let us say, you can also add some ad mixtures for example like phosphate let us say.

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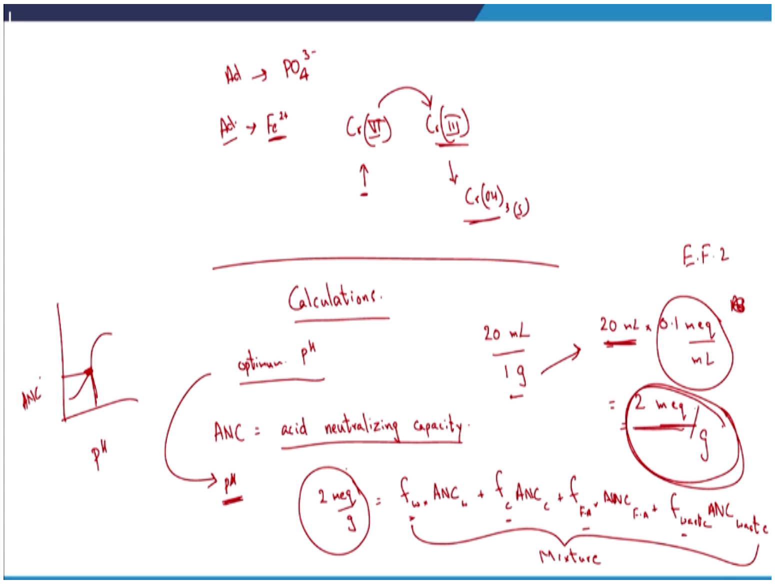

PO43 minus let us say. This what do we say again I believe complexes s not complexes, precipitates out, you know or precipitates lead out, pardon me, right and thus let us say it is not just OH- you dependent upon, but obviously PO43 minus concentration and that increases that optimum range let us say. Similarly, it can precipitate out some of the other heavy metals or you can add iron, let us say, Fe2+ let us say that can degrade, pardon me, reduce chromium from oxidation state 6 to oxidation state 3.

You know that oxidation state 6 is very highly soluble or its mostly wants to stay in the aqueous phase or dissolved in water, but once you use ferrous iron to degrade chromium 6 to chromium 3 as these can be added as the add mixtures and you know that chromium 3 is very less soluble or insoluble and that is going to precipitate out as CrOH thrice solid. Again it is relatively more insoluble compared to chromium 6. So there are different ways to things out.

So now let us move on to calculations, as in we looked at the relevant aspects, how do I go about you know getting the relevant fractions and so on and so forth, right. So let us look at how we get that done now. Obviously the whole key is we want to maintain the optimum pH and the optimum pH is such that even after addition of your extraction fluid or the acetic acid, you are going to have the pH to be high enough such that the metals do not dissolve into the relevant solution now.

So what is the key here, we know that if you look at the TCLP test, we know that we add 20 mL/1 g of waste, right and extraction fluid, if you calculate the relevant aspects and so on let us see what it comes out. We have 20 mL*0.1 mEq/mL, let us say. So that as you can see will be equal to and this is for extraction fluid too, this is the amount of acid, let us say, mEq of acid that you are adding per mL, let us say. What does that equal to, you see that it is 2 Eq or 2 mEq.

So 20 mL*0.1 mEq/mL, so again what is this more or less the amount of H+ that we are putting in, it is the equivalence. We are expressing it in terms of equivalence here. So I am adding 20 mL of extraction fluid per gram, right. So per gram how many equivalence of acid I am adding, its 2 mEq of acid/gram. So that is what I am adding out here, right. So this is from the extraction fluid, you look at the relevant calculations here.

So what is I now, what am trying to say that we are putting an acid at the amount of 2 mEq/gram of your waste. So what characteristics does your acid lead to have now. So not the acid, pardon me, the waste need to have. The waste needs to have an acid neutralizing capacity and how much acid neutralizing capacity should your waste have. It should have 2 mEq/gram of your waste, I mean acid neutralizing capacity.

So we are now going to look at the term acid neutralizing capacity. So I believe you might have or you would probably know or have heard of alkalinity. Alkalinity typically the theoretical equation anyway or definition anyway, you looks at the amount of hydroxide H+, CO32- and HCO3- again what are these more or less bases, OH-, HCO3- and CO32- they are bases. So in effect we are trying to calculate the acid neutralizing capacity of a particular solution when we say alkalinity now.

How do we measure alkalinity now? You take a relevant solution and you take an acid and you titrate it until you reach a particular pH typically 4.3 or 4.5 when you neutralize all the HCO3-2, but if people have HCO3-, but if people want to look at different end points some people choose 7, but again let us not going into that in detail. Typically, we look at 4.5 or 4.3 as an end point, why is that?

We want to see let us say how much acid that the solution can consume, let us say, before reaching to 4.5. So that as you can see the acid neutralizing capacity, but in your case or in our case you know what it should be now. It should be such that or we will look at that such that or we will look at it such that what is the acid neutralizing capacity for our optimum pH.

So you are going to choose the design pH to be your optimum pH that you are going to calculate from your relevant heavy metal based precipitation based data, which we are going to look at again and you are going to look at that. We are going to try to maintain that pH. So if I have a graph as in pH versus the acid neutralizing capacity let us say, I will choose that acid neutralizing capacity for that particular pH.

For example, this is my graph just assume that, so I have to choose this acid neutralizing capacity. But the key is that flyash has its own acid neutralizing capacity. Water might have some of its own acid neutralizing capacity. Cement certainly will have because again cement is relatively higher pH and what else now, I think the waste itself. So you have different aspects that are taken into account, but the total acid neutralizing capacity should end being 2 mEq/gram.

How am I going to get that, it is going to be the fraction of water into acid neutralizing capacity of water plus fraction of cement into acid neutralizing capacity of cement plus fraction of flyash into acid neutralizing capacity of flyash plus fraction of waste into acid neutralizing capacity of waste, again we have an equation here, but what is that we are expressing. So this is the relevant mixture, after solidification and stabilization, these are the different components mixture.

We know that this mixture will be facing or exposed to certain acid. How much acid, we know that the acid will be at 2 mEq/gram, right but you want to see to it that the pH does not fall below a certain pH. So what do I need to do, I need to change these fractions such that the total acid neutralizing capacity will be 2 mEq/gram at that particular pH, right. So that is something to keep in mind and take that forward, right. So obviously what are the other equations that I have that is one equation.

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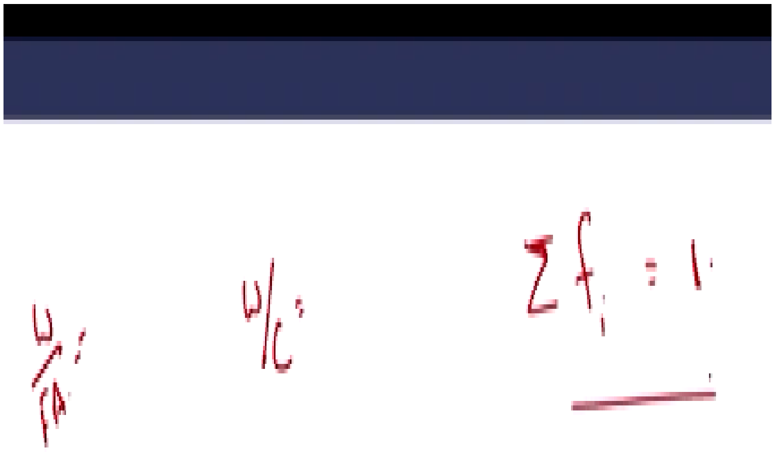

W/FA :

W/C :

$\underline{\sum f_i = 1}$

Typically, I will be having water/cement ratio that is something I will have or water/flyash ratio, these are equations that we typically need to maintain for different reasons, such as structural integrity and obviously another equation is that all the fractions obviously need to be equal some of fractions needs to be equal to 1. It is fraction, so some of all the fractions obviously needs to be equal to 1.

So I guess we are again running out of time. So I will end today session and then we will continue this discussion in the next class and that is it from me for today and thank you.